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Comparisons of Reactivities in Photolysis and Thermolysis Reactions of 1,9-Bis(alkylthio)dibenzothiophenes with Stabilities of Their Dithia Dications in Concentrated Sulfuric Acid

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ABSTRACT

*1,9-Dithia substituents in dibenzothiophenes are in close proximity, being within the van der Waals S–S contact distance (3.70 Å) [1], and hence, these two sulfur atoms affect each other by strong through-space interaction. Cyclic and acyclic dibenzothiophene derivatives bearing two sulfur atoms at the 1,9-positions, such as dibenzothiophene[1,9-fgh][1,5]dithionin (***5***) and 1,9-bis(methylthio)dibenzothiophene (***1a***) and their monosulfoxides* **2a** *and* **6** *were treated with concd sulfuric acid as an oxidizing or deoxygenating reagent to produce the corresponding dithia dications* **7** *and* **3a**. *The dithia dications* **3a** *and* **7** *in concd sulfuric acid gave the monosulfoxides upon treatment with water. On the other hand, a rapid monodealkylation reaction proceeded in the case of 1,9-bis(ethylthio)dibenzothiophene (***1b***) and 1,9-bis(isopropylthio)dibenzothiophene (***1c***) and their monosulfoxides, on dissolution in concd sulfuric acid, afforded high yields of the sequentially dimerized disulfides* **4b** *and* **4c** *after treatment with water. The structure of the dimerized disulfide* **4c** *was determined by X-ray crystallographic analysis, and the following results were obtained: orthorhombic, $P2_12_12_1$, $a = 10.892(1)$ Å, $b = 11.284(2)$ Å, $c = 22.719(3)$ Å, $V = 2792.1(5)$ Å^3, $Z = 4$, $\rho = 1.377$ g/cm^3, μ(MoKa) $= 5.09$ cm^{-1}, $R = 0.030$ ($Rw = 0.030$). In this structure, the four sulfur atoms attached at the 1,9- and 1′,9′-positions of compound* **4c** *are located in an approximately linear arrangement, and the two dibenzothiophene rings are separated by an average intraplanar ring distance of 3.58(8) Å. Furthermore, thermolysis and photolysis of compounds* **1a–c** *were performed, and their reactivities were compared.*

INTRODUCTION

Several dithia and diselena dication salts derived from 1,5-dithia cyclooctane and 1,5-diselena cyclooctane have been isolated in stable crystalline forms, and their structures were determined by X-ray crystallographic analysis [2]. Recently, we have reported that the acyclic dithia and diselena dica-

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Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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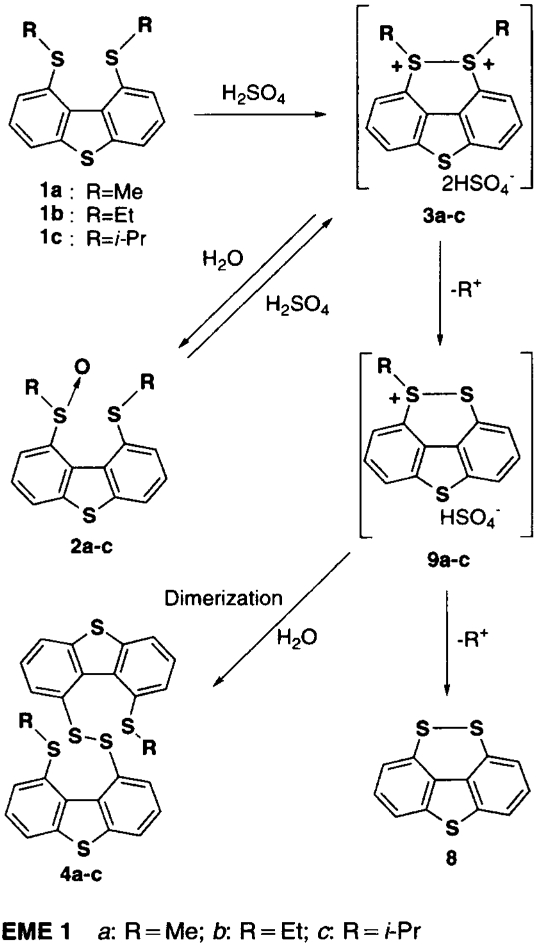
tions derived from 1,9-bis(phenylthio)dibenzothiophene, 1,9-bis(phenylseleno)dibenzothiophene, and 1-(phenylsulfinyl)-9-(phenylthio)dibenzothiophene were generated in concd sulfuric acid and then reacted with water to produce the corresponding sulfoxides and selenoxide in high yields [3]. Furthermore, the magnitude of the through-space interaction between the two sulfur or selenium atoms of 1,9-bis(phenylchalcogeno)dibenzochalcogenophenes influences their photolytic reactivities [4]. However, the stability of dications is influenced by the two alkyl substituents attached to the sulfur atoms in the 1,9-positions. For instance, the dithia dications **3a** and **7** could be observed by ^{1}H-NMR spectroscopy in concd sulfuric acid-d_2, as generated from 1,9-bis(methylthio)dibenzothiophene (**1a**), dibenzothiophene[1,9-*fgh*][1,5]dithionin (**5**), and their monosulfoxides 1-(methylsulfinyl)-9-(methylthio)-dibenzothiophene (**2a**) and dibenzothiophene[1,9-*fgh*][1,5]dithionin 1-oxide (**6**). However, 1,9-bis(ethylthio)dibenzothiophene (**1b**), 1,9-bis-(isopropylthio)dibenzothiophene (**1c**), and their monosulfoxides 1-(ethylsulfinyl)-9-(ethylthio)dibenzothiophene (**2b**) and 1-(isopropylsulfinyl)-9-(isopropylthio)dibenzothiophene (**2c**) were too unstable in concd sulfuric acid-d_2 to allow the detection of the corresponding dithia dications by ^{1}H-NMR spectroscopy. On the other hand, compounds **1b**, **1c**, **2b**, and **2c** were observed by ^{1}H-NMR spectroscopy to produce monodealkylated compounds in concd sulfuric acid-d_2, and their solutions, when treated with water, gave the monodealkylated and the further dimerized disulfides **4b** and **4c**, respectively. Furthermore, different reactivities of compounds **1a–c** were exhibited in their thermolysis and photolysis reactions. This article reports the formation of cyclic and acyclic dithia dications by treating the compounds, **1a** and **5**, and their monosulfoxides, **2a** and **6**, with concd sulfuric acid, and the monodealkylation reaction of compounds **1b**, **1c**, **2b**, and **2c** under identical conditions. The structure of the dimerized disulfide **4c** is reported on the basis of X-ray crystallographic analysis results. Furthermore, the relation between the thermal and photolytic reactivities of compounds **1a–c** and the stabilities of the respective dithia dications in concd sulfuric acid is also reported.

RESULTS AND DISCUSSION

Preparation and Determination of Dithia Dications

In order to determine the through-space interaction between the two sulfur atoms of 1,9-bis(alkylthio)dibenzothiophene derivatives, the formation of dithia dications was examined by treating the compounds **1a–c** and **5** and their monosulfoxides **2a–c** and **6** with concd sulfuric acid, and their detection was carried out by ^{1}H-NMR measurements. When the ^{1}H-NMR spectrum of monosulfoxide **2a** was measured in concd sulfuric acid-d_2, the signal due to the methyl group was observed as only a singlet at δ 3.04, while, in chloroform-d, two singlets appeared at δ 2.33 and δ 2.80. The compound **2a** was treated with concd sulfuric acid for 1 hour and subsequently with water to produce the starting sulfoxide **2a** in 91% yield, together with the monodemethylated and further dimerized disulfide **4a** (4%) and a trace amount of the thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (**8**) [6], revealing that the dithia dication **3a** was produced by the protonation and deoxygenation of the sulfoxide oxygen (Scheme 1) [3]. Similarly, the methyl group of compound **1a** was found by ^{1}H-NMR spectroscopy to give a downfield singlet at δ 3.04 in concd sulfuric acid-d_2. Hence, at least one of the sulfur atoms at the 1,9-positions of



SCHEME 1 *a*: R = Me; *b*: R = Et; *c*: R = *i*-Pr

compound **1a** was oxidized by sulfuric acid. When compound **1a** was treated with concd sulfuric acid for 5 minutes and then with water, the sulfoxide **2a** was obtained in 53% yield, together with the dimerized disulfide **4a** in 34% yield. These results are summarized in Table 1.

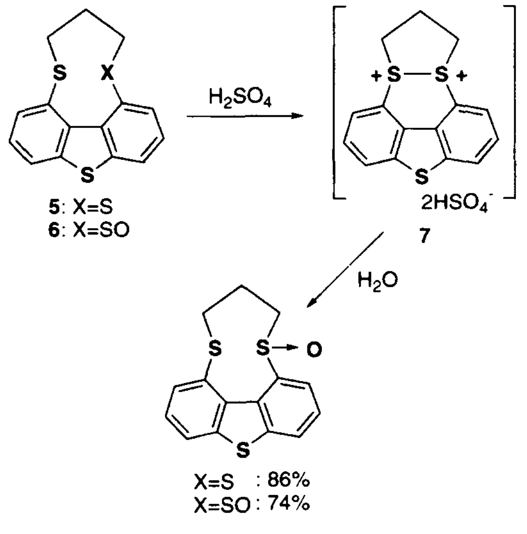
The compounds **1b** and **1c** and their monosulfoxides **2b** and **2c** were unstable in concd sulfuric acid-d_2, and their dithia dications therefore could not be detected at all by ^{1}H-NMR spectroscopy. On the other hand, each of the sulfoxides **2b** and **2c** was found by ^{1}H-NMR spectroscopy to produce the monodealkylated compounds in concd sulfuric acid-d_2, and the respective compounds gradually decomposed in solution. Therefore, compounds **2b** and **2c** were dissolved in concd sulfuric acid, and then the solutions were treated with water to give the monodealkylated and further dimerized disulfides **4b** and **4c** in 60% and 54% yields, respectively, together with compound **8** in 16% and 20% yields. The ^{1}H-NMR spectra of compounds **1b** and **1c** in concd sulfuric acid were found to be similar to those of compounds **2b** and **2c**. The compounds **1b** and **1c** were treated with concd sulfuric acid for 5 minutes and then with water. After the usual workup and separation of the products, the monodealkylated and dimerized disulfides **4b** and **4c** were obtained as the major products in 82% and 84% yields, respectively. However, both the dithia dications and the monodealkylated products of 1,9-bis(methylthio)dibenzofuran (**1d**), 1-(methylsulfinyl)-9-(methylthio)dibenzofuran (**2d**), 1-(methylthio)dibenzothiophene [4], and 2,8-bis(methylthio)dibenzothiophene [4] were not observed by ^{1}H-NMR spectroscopy in concd sulfuric acid-d_2. In addition, these compounds gave a complex mixture when treated with concd sulfuric acid and then water. It has been reported that the dibenzofuran ring of 1,9-bis(phenylthio)dibenzofuran is almost planar, and hence, the through-space interaction between the two sulfur atoms at the 1,9-positions is relatively weak compared with that found in 1,9-bis(phenylthio)dibenzothiophene and 1,9-bis(phenylthio)dibenzoselenophene [3]. These results suggest that a strong through-space interaction between the two sulfur atoms is necessary for the stabilization of the dithia dications and monodealkylated intermediates **9**.

In contrast, compound **5** was obtained in 81% yield from compound **8** after treatment with aminomethanesulfinic acid and 1,3-dibromopropane in tetrahydrofuran. Subsequently, compound **5** was oxidized with one equivalent of *m*-chloroperbenzoic acid (*m*CPBA) to produce compound **6** in 95% yield. Interestingly, when compounds **5** and **6**, respectively, were dissolved in concd sulfuric acid-d_2 in the identical manner described earlier, the ^{1}H and ^{13}C-NMR spectra of these compounds were found to be identical. Furthermore, when compounds **5** and **6**, dissolved in concd sulfuric acid, were treated with water, the monosulfoxide **6** was produced as the major product in 86% and 74% yields, respectively (Scheme 2). This reveals that the dithia dication **7** in these solutions is generated differently compared with the case of compounds **1b** and **1c** and that the cyclic structure is necessary for the stabilization of the dithia dication **7**, except for the methylthio derivative. Furthermore, the dithia dication **7**, generated in concd sulfuric acid, gradually decomposed within a few hours, and the treatment of the solution with water gave an insoluble material.

As shown in Scheme 1, the dimerized disulfides **4a–c** are produced via S–C bond cleavage between a sulfur atom and an alkyl substituent in each of the sulfides **1a–c** and their monosulfoxides **2a–c** and result from the sequential dimerization reaction of the monodealkylated intermediates **9**. The demethyla-

TABLE 1 Reaction of Compounds **2** with Concd Sulfuric Acid

	R	*X*	*Product (%)*					
1a	Me	S	**2a**	53	**4a**	32	**8**	—
1b	Et	S	**2b**	—	**4b**	82	**8**	—
1c	*i*-Pr	S	**2c**	—	**4c**	84	**8**	—
2a	Me	SO	**2a**	91	**4a**	4	**8**	trace
2b	Et	SO	**2b**	—	**4b**	60	**8**	16
2c	*i*-Pr	SO	**2c**	—	**4c**	54	**8**	20

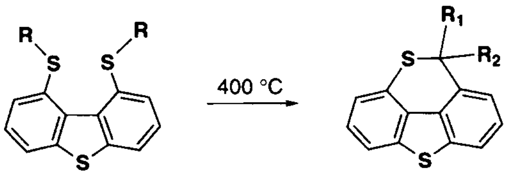


SCHEME 2

tion reaction of compounds **1a** and **2a** should proceed by an initial formation of dithia dication **3a** from either a homolytic cleavage of the S–C bond at the methylthio group or from a nucleophilic substitution reaction at the methyl carbon atom upon treatment with water or sulfuric acid. Meanwhile, the monodealkylation of compounds **1b** and **1c** and their monosulfoxides **2b** and **2c** may also proceed via the corresponding dithia dications, **3b** and **3c**, which could not be detected by ^{1}H-NMR spectroscopy in concd sulfuric acid-d_2, because the dealkylation reaction was observed for compounds **1b**, **1c**, **2b**, and **2c** under similar conditions (Scheme 1). Since ^{1}H-NMR spectra in concd sulfuric acid-d_2 showed that compounds **1b**, **1c**, **2b**, and **2c** formed monodealkylated intermediates **9** and that their solutions, when treated with water, produced the dimerized disulfides **4b** and **4c**, then it follows that the dealkylation and dimerization reactions of compounds **1a–c** and **2a–c** should proceed via dithia dications **3b**, **3c**, and the thiasulfonium-like intermediate **9**, which reductively dimerizes to produce disulfides **4a–c**. It has been known that the NMR spectrum is influenced by a magnetic moment of a radical or a cation radical that gives broad signals in the NMR spectrum. Since the intermediates **9** were observed by ^{1}H-NMR spectroscopy, these dealkylation reactions may proceed via the nucleophilic reaction as previously described (Scheme 1).

Thermolysis and Photolysis of Compounds 1a–c

The photolytic desulfurization reactions of 1,9-bis(phenylthio)dibenzochalcogenophenes are influenced by a repulsive force between the two sulfur atoms at the 1,9-positions and are related to the stabilities of the dithia dications [3]. Following the thermolysis of compound **1c** at 400°C for 15 minutes, the desulfurized and cyclized product, 9,9-dimethyl-9*H*-thieno[2,3,4,5-*lmn*][9]thiaphenanthrene (**10c**), was obtained in 87% yield (Scheme 3). However, after similar thermolyses of **1a** (90 minutes) and **1b** (60 minutes), 9*H*-thieno[2,3,4,5-*lmn*][9]thiaphenanthrene (**10a**) and 9-methyl-9*H*-thieno[2,3,4,5-*lmn*][9]thiaphenanthrene (**10b**), respectively, were produced in only 26% and 57% yields. On the photolysis of compounds **1b** and **1c** with a 400 W high-pressure mercury lamp in benzene for 12 hours, the S–C bond cleavage reactions proceeded mainly between sulfur and the alkyl groups to produce the dimerized disulfides **4b** and **4c**, respectively, in 17% and 45% yields. However, only a low photochemical reactivity was observed for compound **1a** as compared with **1b** and **1c**. In the photolysis of **1a**, the S–C bond fission between sulfur and the methyl group proceeded slowly to give the dimerized disulfides **4a** in 1% yield, together with recovery of the starting **1a** (69%) [4]. Meanwhile, the photolysis of 1-(isopropylthio)dibenzothiophene (**11c**), 1-(phenylthio)-dibenzothiophene, and 2,8-bis(phenylthio)-dibenzothiophene did not proceed under similar conditions, and the starting compounds were recovered quantitatively. These results suggest that the stabilities of the dithia dications and the photolytic and the thermolytic reactivities are all influenced by the strength of the S–C bonds between the alkyl substituents and the respective sulfur atoms. The photolytic and thermolytic reactivities of compounds **1a–c** decreased in the order **1c** > **1b** > **1a**.



1a : R=Me : 90 min
1b : R=Et : 60 min
1c : R=*i*-Pr : 15 min

10a: R_1=R_2=H : 26%
10b: R_1=H, R_2=Me : 57%
10c: R_1=R_2=Me : 87%

SCHEME 3

X-ray Crystallographic Analysis of Compound 4c

The only structure that could be determined by single-crystal X-ray crystallographic analysis was **4c**, since compounds **4a** and **4b** did not give suitable crystalline forms necessary for X-ray analysis. Compound **4c** crystallized in the orthorhombic system with the cell parameters and calculated cell volume, a = 10.892(1) Å, b = 11.284(2) Å, c = 22.719(3) Å, and V = 2792.1(5) Å^3. The calculated density is 1.377 g/cm^3 for Z = 4, and the formular weight is 578.90. The space group was determined to be $P2_12_12_1$ from the systematic absences: *h, 0, 0*: *h* = *2n*; *0, k, 0*: *k* = *2n*; *0, 0, l*: *l* = *2n*. The linear absorption coefficient is 5.09 cm^{-1} for MoK$\alpha_{1,2}$ radiation. The structure was solved by the direct method. The 2690 reflections having intensities greater than 5.0 times their standard deviation were used in the refinements. The final cycle of refinement included 403 variable parameters and converged with unweighted and weighted agreement factors of R = 0.030 and R_W = 0.030, respectively.

The structure exhibits a twofold noncrystallographic axis of symmetry; i.e., it is not on a special symmetry position. The molecular structure and the adopted numbering scheme are illustrated by an ORTEP plot shown in Figure 1. The two dibenzothiophene ring systems of compound **4c** are separated by an average intraplanar dibenzothiophene dis-

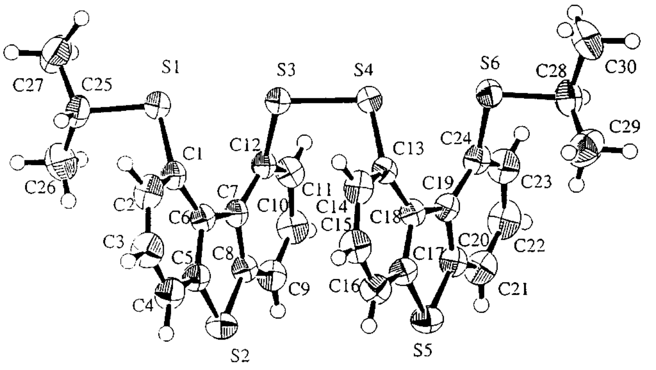


FIGURE 1 The ORTEP drawing of compound **4c**.

tance of 3.53(8) Å. The dihedral angles between the pairs of least-squares planes defined by the carbon atoms, C(1) to C(6) and C(7) to C(12), and C(13) to C(18) and C(19) to C(24), are 15.3(4)° and 15.1(4)°, and the torsion angles at C(1)–C(6)–C(7)–C(12) and C(13)–C(18)–C(19)–C(24) are 22.1(7)° and 22.5(7)°, suggesting that these dibenzothiophene rings are distorted from the normal planar form [8] by the repulsion between S(1) and S(3) atoms and S(4) and S(6) atoms. The S(3)–S(4) bond connecting the two halves of the molecule is 2.089(1) Å in length, and the torsion angle C(12)–S(3)–S(4)–C(13) is −54.5(2)°. Interestingly, the two sulfur atoms S(1) and S(6) contact S(3) and S(4), respectively, by distances of 2.950(1) Å and 2.920(1) Å, which are significantly less than the sum of the van der Waals radii [1]. Furthermore, the angles at S(1)–S(3)–S(4) and S(3)–S(4)–S(6) positions and torsion angle at S(1)–S(3)–S(4)–S(6) are 161.52(6)°, 161.29(6)°, and 178.5(1)°. Though the two sulfur atoms S(1) and S(6) deviate from the line passing through S(3) and S(4) by an average angle 18.7(1)°, these four sulfur atoms should interact strongly in a linear structure.

Electrochemical Properties and UV Spectra of Dibenzothiophenes

The intensity of electrostatic interaction between two heteroatoms can be estimated by measuring spectroscopic and physical properties, such as NMR, UV, and oxidation potentials. Particularly, the oxidation potentials and UV absorption maxima can be employed for diagnosis of the displacement of electrons from the heteroatoms in the molecule. To estimate the electronic interaction between the two sulfur atoms at the 1,9-positions, the oxidation potentials and UV spectra of **1a–d** and **5** were measured and compared with those of the respective monosubstituted derivatives **11a–d**. As shown in Table 2, compounds **1a–c** have lower oxidation potentials and absorb longer wavelength light in UV spectra than those of the corresponding monosubstituted derivatives **11a–c** and the dibenzofuran derivative **1d**. On the other hand, compound **5**, bearing a rigid structure as compared with compounds **1a–d**, shows a reversible cyclic voltammogram different from those of compounds **1a–d** and **11a–d**. Hence, the dithia dication **7**, generated in concd sulfuric acid, is stable in a different manner compared with the cases of **1b** and **1c**, and the cyclic structure is necessary for the stabilization of the dithia dication, except for **3a**. These results suggested that the through-space interaction between the two sulfur atoms plays an important part during the formation and for the stabilization of the dithia dications, as well as for promoting the monodealkylation and the subsequent dimerization reactions in sulfuric acid solutions, and the proximate effect between the two alkylthio substituents is apparently essential for initiation of these photolytic and thermolytic reactions.

CONCLUSIONS

The stabilities of the dications were found to be influenced by the nature of the alkyl substituents attached to each of the sulfur atoms at the 1,9-positions. For instance, dithia dications **3a** and **7** generated from compounds **1a**, **5**, **2a**, and **6** could be observed by ^{1}H-NMR spectroscopy in concd sulfuric acid-d_2. However, compounds **1b**, **1c**, **2b**, and **2c** were too unstable in concd sulfuric acid-d_2 to allow the detection of the respective dithia dications by ^{1}H-NMR spectroscopy, but when converted to the monodealkylated intermediate **9**, detectable by ^{1}H-NMR spectroscopy, which on treatment with water, yielded the monodealkylated and the further dimerized disulfides **4b** and **4c**. Furthermore, the compounds **1a–c** exhibited different reactivities when undergoing thermolysis and photolysis reactions.

TABLE 2 Oxidation Potentials (*V*) and UV Spectra of Several Dibenzochalcogenophenes

		UV	
	Ep(V)	λ_{max}(nm), (CH_2Cl_2)	
1a	0.76	357	361
1b	0.68	346	360
1c	0.70	346	360
1d	0.94	322	333(sh)
5	0.46[a]	348	385
11a	1.02	325	338
11b	0.95	325	340
11c	0.99	326	338
11d	1.07	307	319

[a] Since the cyclic voltammogram was reversible, the oxidation potential was shown in $E_{1/2}$.

EXPERIMENTAL SECTION

General

The IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. The NMR spectra were measured on a JEOL JNM-EX270, a Bruker AM-500, and a Bruker AC-400 spectrometer. Mass spectra were obtained with a JEOL JMX SX102 and a Shimadzu QP-2000 mass spectrometer. The UV spectra were measured with a Hitachi U-3000 spectrometer. The X-ray data collection was performed on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer (23 ± 1°C), and all calculations were performed using the teXsan crystallographic software package [6]. For determination of the oxidation potential, a Hokuto Denko Co. Model HB-104 apparatus was used.

Measurement of Oxidation Potentials

The oxidation potential of each compound was measured by cyclic voltammetry in acetonitrile at 20°C, using a Pt electrode, a glassy carbon electrode, and Ag/0.01 M $AgNO_3$ as a reference electrode (electrolyte: 0.1 M $NaClO_4$; scan rate: 200 mV/s).

PREPARATION

4,6-Bis(ethylthio)thianthrene 5-Oxide

Thianthrene 5-oxide (5.00 g, 21.5 mmol) dissolved in THF (100 mL) was lithiated with 0.473 M LDA (150 mL, 71 mmol) for 3 hours at −78°C. To this solution, elemental sulfur (3.5 g, 108 mmol) was added, and the mixture was stirred for 3 hours at −20°C. Then ethyl iodide (14 mL, 172 mmol) was added dropwise, and the solution was stirred for 10 hours at 25°C. After treatment with water (5 mL), the solvent was evaporated, and the aqueous solution was extracted with CH_2Cl_2 (3 × 200 mL). The extract was washed with a saturated solution of $Na_2S_2O_3$, followed by water, and dried with $MgSO_4$. The residue was purified by column chromatography (silica gel, CH_2Cl_2:ethyl acetate = 5:1) and by recrystallization from ethanol to give 4,6-bis(ethylthio)thianthrene 5-oxide (6.0 g, 80%); mp 133–133.5°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.38 (t, J = 7.3 Hz, 6H, CH_3), 3.08 (q, J = 7.3 Hz, 4H, CH_2), 7.38 (t, J = 7.6 Hz, 2H), 7.43 (dd, J = 7.6, 1.6 Hz, 2H), 7.58 (dd, J = 7.6, 1.6 Hz, 2H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 14.1, 29.5, 126.1, 128.3, 130.7, 134.7, 136.7, 140.4; IR (KBr) 1031 cm^{-1}; MS (m/z) 320 (M^+); anal. calcd for $C_{16}H_{16}OS_4$: C, 54.51; H, 4.57. Found: C, 54.48; H, 4.52.

4,6-Bis(isopropylthio)thianthrene 5-Oxide

Thianthrene 5-oxide (5.00 g, 21.5 mmol, in 80 mL of THF) was treated similarly with 0.284 M LDA (250 mL, 71 mmol), elemental sulfur (8.0 g, 267 mmol), and isopropyl iodide (21.5 mL, 215 mmol). After identical workup and purification, 4,6-bis(isopropylthio)thianthrene 5-oxide was obtained (5.9 g, 72%); mp 115–116°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.33 (d, J = 6.7 Hz, 6H, CH_3), 1.42 (d, J = 6.7, 6H, CH_3), 3.53 (sept, J = 6.7 Hz, 2H, CH), 7.39 (t, J = 7.8 Hz, 2H), 7.53 (dd, J = 7.8, 1.3 Hz, 2H), 7.65 (dd, J = 7.8, 1.3 Hz, 2H); IR (KBr) 1031 cm^{-1}; MS (m/z) 380 (M^+); anal. calcd for $C_{18}H_{20}OS_4$: C, 56.80; H, 5.30. Found: C, 56.62; H, 5.13.

1,9-Bis(methylthio)dibenzothiophene (**1a**) *and 1,9-Bis(methylthio)dibenzofuran* (**1d**)

These compounds were prepared from 4,6-bis(methylthio)thianthrene 5-oxide and 1,9-bis(methylthio)phnoxathiin 10-oxide [3,5c].

1,9-Bis(ethylthio)dibenzothiophene (**1b**)

To a THF (300 mL) solution of 1,9-bis(ethylthio)thianthrene 5-oxide (4.80 g, 13.7 mmol), 1.37 M C_2H_5MgBr/THF (100 mL, 137 mmol) was added dropwise. The solution was stirred for 3 hours, anhydrous $CuCl_2$ (27.6 g, 206 mmol) added, and then the solution was stirred further for 36 hours. The solution was treated with water (5 mL) and then with a saturated NH_4Cl solution. After evaporation of the solvent, the residue was treated with a 2N NaOH solution and subsequently extracted with CH_2Cl_2 (3 × 200 mL). The extract was dried with $MgSO_4$, and then the solvent was evaporated. The residue was purified by column chromatography (silica gel, CCl_4) and by recrystallization (*n*-hexane:cyclohexane = 1:1) to give **1b** (3.0 g, 71%); mp 92–92.5°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 6H), 2.77 (q, J = 7.4 Hz, 4H), 7.43 (t, J = 7.9 Hz, 2H), 7.63 (dd, J = 7.9, 1.0 Hz, 2H), 7.69 (dd, J = 7.9, 1.0 Hz, 2H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 14.1, 33.5, 120.3, 126.9, 129.2, 134.8, 136.6, 140.0; MS (m/z) 304 (M^+); anal. calcd for $C_{16}H_{16}S_3$: C, 63.11; H, 5.30. Found: C, 63.28; H, 5.25.

1,9-Bis(isopropylthio)dibenzothiophene (**1c**)

1,9-Bis(isopropylthio)thianthrene 5-oxide (3.8 g, 10 mmol) was treated with 1.0 M C_2H_5MgBr/THF (100 mL, 100 mmol) and anhydrous $CuCl_2$ (20.2 g, 150 mmol) similarly as described earlier. After identical workup and purification, compound **1c** was obtained (2.5 g, 76%); mp 117–118°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (d, J = 6.5 Hz, 12 H), 3.11 (sept, J = 6.5 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.68 (dd, J = 7.8, 1.1 Hz, 2H), 7.72 (dd, J = 7.8, 1.1 Hz, 2H);

^{13}C NMR (67 MHz, $CDCl_3$) δ 22.6, 43.3, 120.7, 126.8, 130.8, 134.1, 137.7, 139.8; MS (*m*/*z*) 332 (M^+); anal. calcd for $C_{18}H_{20}S_3$: C, 65.01; H, 6.06. Found: C, 64.67; H, 6.03.

1-(Isopropylsulfinyl)-9-(isopropylthio)dibenzothiophene (2c)

To a solution of **1c** (498 mg, 1.5 mmol) in 100 mL of CH_2Cl_2, *m*CPBA (370 mg, 1.5 mmol, assay ≥ 60%) in 50 mL of CH_2Cl_2 was added gradually for 2 hours at −20°C. The solution was stirred for 1 hour at −20°C and treated with NH_3 gas. After filtration, the solution was evaporated, and the residue was purified by column chromatography (silica gel; CH_2Cl_2:ethyl acetate = 1:1) to give **2c** (343 mg, 66%); mp 107–108°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.42 (d, *J* = 6.5 Hz, 3H, CH_3), 0.82 (d, *J* = 6.5 Hz, 3H, CH_3), 1.20 (d, *J* = 6.5 Hz, 3H, CH_3), 1.38 (d, *J* = 6.5 Hz, 3H, CH_3), 2.86 (sept, *J* = 6.5 Hz, 1H, CH) 2.96 (sept, *J* = 6.5 Hz, 1H, CH), 7.47 (t, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.29 (dd, *J* = 7.8, 1.4 Hz, 1H); IR (KBr) 1046 cm^{-1} (SO); MS (*m*/*z*) 348 (M^+); anal. calcd for $C_{18}H_{20}OS_3$: C, 62.03; H, 5.78. Found: C, 61.92; H, 5.76.

1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (2a)

Compound **2a** was obtained by the treatment of **1a** with *m*CPBA [3]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.80 (s, 3H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.70 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.81 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.99 (dd, *J* = 7.8, 0.8 Hz, 1H), 8.36 (dd, *J* = 7.8, 0.9 Hz, 1H).

1-(Ethylsulfinyl)-9-(ethylthio)dibenzothiophene (2b)

Compound **1b** (304 mg, 1 mmol) was treated with *m*CPBA (276 mg, 1 mmol, assay ≥ 60%) similarly to give **2b** (292 mg, 91%); mp 47.5–48°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.4 Hz, 3H, CH_3), 1.17 (t, *J* = 7.4 Hz, 3H, CH_3), 2.54 (dq, *J* = 7.4, 5.8 Hz, 1H, CH_2), 2.58 (dq, *J* = 7.4, 5.3 Hz, 1H, CH_2), 2.71 (dq, *J* = 7.4, 5.3 Hz, 1H, CH_2), 3.15 (dq, *J* = 7.4, 5.8 Hz, 1H, CH_2), 7.47 (t, *J* = 7.8 Hz, 1H), 7.73 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.85 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.99 (dd, *J* = 7.8, 0.9 Hz, 1H), 8.33 (dd, *J* = 7.8, 0.9 Hz, 1H); IR (KBr) 1040 cm^{-1} (SO); MS (*m*/*z*) 320 (M^+); anal. calcd for $C_{16}H_{16}OS_3$: C, 59.96; H, 5.03. Found: C, 59.90; H, 4.79.

1-(Methylsulfinyl)-9-(methylthio)dibenzofuran (2d)

1,9-Bis(methylthio)dibenzofuran (100 mg, 0.38 mmol) was oxidized with *m*CPBA (120 mg, 0.38 mmol, assay ≥ 55%) in a manner similar to that described earlier to give **2d** (97 mg, 91%); mp 141–143°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.58 (s, 3H), 2.82 (s, 3H), 7.48–7.55 (m, 3H), 7.59–7.71 (m, 2H), 8.24–8.28 (m, 1H); IR (KBr) 1040 cm^{-1} (SO); MS (*m*/*z*) 276 (M^+); anal. calcd for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38. Found: C, 60.57; H, 4.36.

Dibenzothiophene[1,9-fgh][1,5]dithionine (5)

Thieno[2,3,4,5-*lmn*][9,10]dithiaphenanthrene (246 mg, 1.0 mmol), aminomethansulfinic acid (200 mg, 1.8 mmol), and cetylammonium bromide (40 mg, 0.1 mmol) were dissolved in a solution of THF and H_2O (THF 40 wt%), and a NaOH solution (3.7 M, 20 mL) was added to the mixture. The solution was refluxed, and 1,3-dibromopropane (0.1 mL, 1.0 mmol in 30 mL THF) was added slowly over a period of 2.5 hours. The solution was refluxed for an additional 1 hour, and then the solution was extracted with CH_2Cl_2 (3 × 100 mL) after having been cooled. The extract was dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2) and by recrystallization (*n*-hexane) to give **5** (223 mg, 81%); mp 88.5–89°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.94 (quint, *J* = 6.1 Hz, 2H, CH_2), 3.25 (t, *J* = 6.1 Hz, 4H, SCH_2), 7.37 (t, *J* = 7.6 Hz, 2H), 7.78 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.82 (dd, *J* = 7.6, 1.3 Hz, 2H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 24.0, 36.5, 122.4, 126.3, 133.4, 135.1, 137.3, 141.4; MS (*m*/*z*) 288 (M^+); anal. calcd for $C_{15}H_{12}S_3$: C, 62.46; H, 4.19. Found: C, 62.51; H, 4.07.

Dibenzothiophene[1,9-fgh][1,5]dithionin 1-Oxide (6)

Compound **5** (50 mg, 0.17 mmol) was dissolved in CH_2Cl_2 (50 mL), and the solution was cooled to −20°C. To this solution, *m*CPBA (30 mg, 0.17 mmol in 30 mL of CH_2Cl_2) was added, and the solution was stirred for 1 hour. NH_3 gas was bubbled into the solution, and the white precipitate that had formed was filtered off. The filtrate was evaporated, and the residue was purified by column chromatography (silica gel, CH_2Cl_2:ethyl acetate = 1:1) to give **6** (50 mg, 95%); mp 211.5–212°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.73–1.96 (m, 1H, CH_2), 2.08–2.27 (m, 1H, CH_2), 2.68–2.96 (m, 2H, CH_2), 2.97–3.13 (m, 1H, CH_2), 3.42–3.60 (m, 1H, CH_2), 7.40 (t, *J* = 7.9 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.95 (dd, *J*

= 7.9, 1.3 Hz, 1H), 8.51 (dd, *J* = 7.9, 1.3 Hz, 1H); IR (KBr) 1029 cm^{-1}; MS (*m/z*) 304 (M$^+$); anal. calcd for $C_{15}H_{12}OS_3$: C, 59.18; H, 3.97. Found: C, 59.15; H, 3.93.

1-(Ethylthio)dibenzothiophene (**11b**)

To a THF (25 mL) solution of compound **2b** (200 mg, 0.63 mmol), 0.126 M C_2H_5MgBr/THF (50 mL, 6.3 mmol) was added dropwise. The solution was stirred for 3 hours and was then treated with water (5 mL). After evaporation of the solvent, the residue was extracted with CH_2Cl_2 (3 × 50 mL). The extract was dried with $MgSO_4$, and then the solvent was evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2) and then by preparative HPLC to give **11b** as a colorless liquid (96 mg, 64%); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.4 Hz, 3H), 3.05 (q, *J* = 7.4 Hz, 2H), 7.28–7.53 (m, 4H), 7.65–7.73 (m, 1H), 7.79–7.88 (m, 1H), 9.09–9.18 (m, 1H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 14.0, 27.9, 120.4, 122.3, 124.1, 125.8, 125.9, 126.2, 126.6, 133.4, 133.8, 135.9, 139.4, 140.5; MS (*m/z*) 244 (M$^+$).

1-(Isopropylthio)dibenzothiophene (**11c**)

Compound **2c** (174 mg, 0.5 mmol) was treated with 0.5 M C_2H_5MgBr/THF (10 mL, 5 mmol) similarly to give **11c** as a light-yellow liquid (91 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (d, *J* = 6.7 Hz, 6 H), 3.47 (sept, *J* = 6.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.42–7.50 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.82–7.87 (m, 1H), 9.27–9.33 (m, 1H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 23.0, 38.5, 121.7, 122.4, 124.0, 125.9, 126.4, 126.7, 130.3, 132.5, 134.9, 136.0, 139.6, 140.6; MS (*m/z*) 258 (M$^+$).

^{1}H-NMR Spectrum of Compound **2a** *in D_2SO_4*

^{1}H NMR (500 MHz, D_2SO_4, DSS) δ 3.04 (s, 6H, CH_3), 7.59 (t, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H).

^{1}H-NMR Spectrum of Compound **2b** *in D_2SO_4*

^{1}H NMR (400 MHz, D_2SO_4, DSS) δ 0.76 (t, *J* = 7.3 Hz, 3H), 2.84 (q, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H).

^{1}H-NMR Spectrum of Compound **2c** *in D_2SO_4*

^{1}H NMR (400 MHz, D_2SO_4, DSS) δ 0.64 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 3.14 (sept, *J* = 6.7 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.31–7.38 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.81–7.87 (m, 1H).

^{1}H and ^{13}C-NMR Spectra of Compounds **5** *and* **6** *in D_2SO_4*

^{1}H NMR (270 MHz, D_2SO_4, DSS) δ 2.23–2.56 (m, 1H, CH_2), 3.03–3.16 (m, 1H, CH_2), 3.99–4.43 (m, 4H, CH_2), 7.46–8.16 (m, 6H); ^{13}C NMR (67 MHz, D_2SO_4, DSS) δ 40.2, 65.1, 122.1, 127.1, 128.6, 134.2, 134.4, 147.7.

Reaction of Compound **1a** *with Concd H_2SO_4*

Compound **1a** (50 mg, 0.18 mmol) was dissolved in concd H_2SO_4 (1 mL), and the solution was stirred for 5 minutes. Then the solution was poured into ice water. The solution was neutralized with NaOH solution and extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2 and CH_2Cl_2:ethyl acetate = 1:1) and preparative HPLC to give **4a** (16 mg, 34%) and **2a** (28 mg, 53%); **4a**: mp 194–196°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.29 (s, 6H), 6.79 (t, *J* = 7.7 Hz, 2H), 7.24 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 7.7, 1.1 Hz, 2H) 7.50 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.64 (dd, *J* = 7.7, 1.1 Hz, 2H); MS (*m/z*) 490 (M$^+$ − 32); anal. calcd for $C_{26}H_{18}S_6$: C, 59.73; H, 3.47. Found: C, 59.61; H, 3.41.

Reaction of Compound **1b** *with Concd H_2SO_4*

Compound **1b** (50 mg, 0.16 mmol) was treated with concd H_2SO_4 (1 mL) for 5 minutes to give **4b** (25 mg, 84%); mp 142–144°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.4 Hz, 6H), 2.63 (q, *J* = 7.4 Hz, 4H), 6.73 (t, *J* = 7.7 Hz, 21H), 7.21 (dd, *J* = 7.7, 0.8 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 7.7, 0.8 Hz, 2H), 7.54 (dd, *J* = 7.7, 0.8 Hz, 2H), 7.67 (dd, *J* = 7.7, 0.8 Hz, 2H); MS (*m/z*) 518 (M$^+$ − 32); anal. calcd for $C_{28}H_{22}S_6$: C, 61.05; H, 4.03. Found: C, 60.89; H, 3.98.

Reaction of Compound **1c** *with Concd H_2SO_4*

Compound **1c** (35 mg, 0.11 mmol) was treated with concd H_2SO_4 (1 mL) for 5 minutes similarly to give **4c** (25 mg, 84%); mp 178–180°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.78 (d, *J* = 6.7 Hz, 12H), 2.87 (sept, *J* = 6.7 Hz, 2H), 6.67 (t, *J* = 7.7 Hz, 2H), 7.17 (dd, *J* = 7.7, 0.9 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.42 (dd, *J* = 7.7, 0.9 Hz, 2H), 7.57 (dd, *J* = 7.7, 0.9 Hz, 2H), 7.70 (dd, *J* = 7.7, 0.9 Hz, 2H); MS (*m/z*) 578 (M$^+$);

anal. calcd for $C_{30}H_{26}S_6$: C, 62.24; H, 4.53. Found: C, 61.60; H, 4.67.

Reaction of Compound **2a** *with Concd H_2SO_4*

Compound **2a** (149 mg, 0.51 mmol) was treated with concd H_2SO_4 (5 mL) for 1 hour. After identical workup, the residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:ethyl acetate = 1:1 for **2a**, *n*-hexane for **4a** and **8**) to produce **2a** (136 mg, 91%), **4a** (5 mg, 4%), and a trace amount of **8** [7].

Reaction of Compound **2b** *with Concd H_2SO_4*

Compound **2b** (33 mg, 0.1 mmol) was treated with concd H_2SO_4 (2 mL) for 10 minutes similarly to produce **4b** (17 mg, 60%) and **8** (7 mg, 16%).

Reaction of Compound **2c** *with Concd H_2SO_4*

Compound **2c** (72 mg, 0.22 mmol) was treated with concd H_2SO_4 (2 mL) for 30 minutes to give **4c** (32 mg, 54%) and **8** (10 mg, 20%).

Reaction of Compound **5** *with Concd H_2SO_4*

Compound **5** (50 mg, 0.18 mmol) was treated with concd H_2SO_4 (1 mL) for 5 minutes. After identical workup, the residue was purified by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2:ethyl acetate = 1:1) to give **6** (46 mg, 86%).

Reaction of Compound **6** *with Concd H_2SO_4*

Compound **6** (25 mg, 0.08 mmol) was treated with concd H_2SO_4 (1 mL) for 5 minutes to produce **6** (18 mg, 74%).

Photolysis of Compound **1c**

Compound **1c** (100 mg, 0.3 mmol) in 10 mL of benzene was irradiated with a 400 W high-pressure mercury lamp for 12 hours. After distillation of the solvent, the residue was purified by column chromatography (silica gel; CH_2Cl_2) and preparative HPLC, giving compound **4c** in 45% (39 mg).

Photolysis of Compounds **1a** *and* **1b**

Compounds **1a** and **1b** were treated in a similar manner to that described earlier to produce **4a** and **4b** in 1% and 17% yields, respectively.

Thermolysis of Compound **1c**

Compound **1c** (201 mg, 0.6 mmol) was placed in a Pyrex tube and heated at 400°C with an electric furnace for 15 minutes. The reaction mixture was extracted with CH_2Cl_2. After purification by column chromatography (silica gel; CH_2Cl_2) and preparative HPLC, **10c** was obtained in 87% (135 mg) yield together with dibenzo[*bc*,*fg*][1,4]dithiapentalene (trace) and **8** (9%); **10c**: mp 95–95.5°C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.80 (s, 6H), 7.22 (d, J = 7.7 Hz, 1H), 7.35 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 48.4, 117.7, 118.6, 120.5, 120.9, 127.5, 127.9, 130.3, 130.5, 131.0, 138.4, 138.5, 139.3; MS (*m*/*z*) 256 (M^+); anal. calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72. Found: C, 70.13; H, 4.65.

Thermolysis of Compound **1a**

Compound **1a** was treated in a similar manner to that described earlier for 90 minutes. After identical purification, **10a** was obtained in 26% yield together with dibenzo[*bc*,*fg*][1,4]dithiapentalene (trace) and **8** (7%); **10a**: mp 118–119°C; ^1H NMR (500 MHz, $CDCl_3$) δ 4.46 (s, 2H), 7.17 (d, J = 7.7 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H); MS (*m*/*z*) 227 ($M^+ - 1$); anal. calcd for $C_{13}H_8S_2$: C, 68.38; H, 3.53. Found: C, 68.11; H, 3.45.

Thermolysis of Compound **1b**

Compound **1b** was treated as described for **1c** for 60 minutes to produce **10b** in 57% yield together with dibenzo[*bc*,*fg*][1,4]dithiapentalene (trace) and **8** (8%); **10b**: mp 68–69°C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.67 (d, J = 6.9 Hz, 3H), 4.66 (q, J = 6.9 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.21 (dd, J = 7.9, 0.7 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.44 (t, J = 7.9 Hz, 1H), 7.57 (dd, J = 7.9, 0.7 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 25.1, 40.3 118.7, 120.6, 120.7, 121.0, 127.7, 127.7, 129.3, 129.7, 130.9, 133.5, 138.9, 139.2; MS (*m*/*z*) 242 (M^+); anal. calcd for $C_{14}H_{10}S_2$: C, 69.32; H, 4.13. Found: C, 69.12; H, 4.65.

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REFERENCES

[1] I. Hargittai, B. Rozsondai: in S. Patai, Z. Rappoport, (eds): *The Chemistry of Organic Selenium and Tellurium*

Compounds, Volume 1, John Wiley and Sons, New York, p. 63 (1986).

[2] H. Fujihara, N. Furukawa, *J. Mol. Struct. (Theochem.), 186,* 1988, 261; W. K. Musker, *Acc. Chem. Res., 13,* **1980**, 200; W. K. Musker, T. L. Wolford, P. B. Roush, *J. Am. Chem. Soc., 100,* **1978**, 6416; H. Fujihara, R. Akaishi, N. Furukawa, *J. Chem. Soc. Chem. Commun.,* **1987**, 930; F. Iwasaki, N. Toyoda, R. Akaishi, H. Fujihara, N. Furukawa, *Bull. Chem. Soc. Jpn., 61,* **1988**, 2563; H. Fujihara, R. Akaishi, N. Furukawa, *Tetrahedron Lett., 30,* **1989**, 4399; H. Fujihara, R. Akaishi, T. Erata, N. Furukawa, *J. Chem. Soc. Chem. Commun.,* **1989**, 1789.

[3] T. Kimura, Y. Horie, S. Ogawa, H. Fujihara, F. Iwasaki, N. Furukawa, *Heterocycles, 33,* **1992**, 101; N. Furukawa, T. Kimura, N. Horie, S. Ogawa, H. Fujihara, *Tetrahedron Lett., 33,* **1992**, 1489; N. Furukawa, Y. Ishikawa, T. Kimura, S. Ogawa, *Chem. Lett.,* **1992**, 675; T. Kimura, Y. Horie, S. Ogawa, N. Furukawa, *Heteroatom Chemistry, 4,* **1993**, 243.

[4] T. Kimura, Y. Ishikawa, N. Furukawa, *Heterocycles, 35,* **1993**, 53; T. Kimura, Y. Ishikawa, K. Ueki, Y. Horie, N. Furukawa, *J. Org. Chem., 59,* **1994**, 7117; T. Kimura, N. Furukawa, *Tetrahedron Lett., 36,* **1995**, 1079.

[5] (a) T. Kimura, Y. Ishikawa, S. Ogawa, T. Nishio, I. Iida, N. Furukawa, *Tetrahedron Lett., 33,* **1992**, 6355; (b) T. Kimura, Y. Ishikawa, N. Furukawa, *Chem. Lett.,* **1993**, 635; (c) T. Kimura, Y. Ishikawa, Y. Minoshima, N. Furukawa, *Heterocycles, 37,* **1994**, 541.

[6] teXsan Structure Analysis Package, Molecular Structure Corp. (1985 and 1992).

[7] S. Cossu, O. De Lucchi, E. Piga, G. Valle, *Phosphorus, Sulfur and Silicon, 63,* **1991**, 51.

[8] R. M. Schaffrin, J. Trotter, *J. Chem. Soc. (A),* **1970**, 1561.